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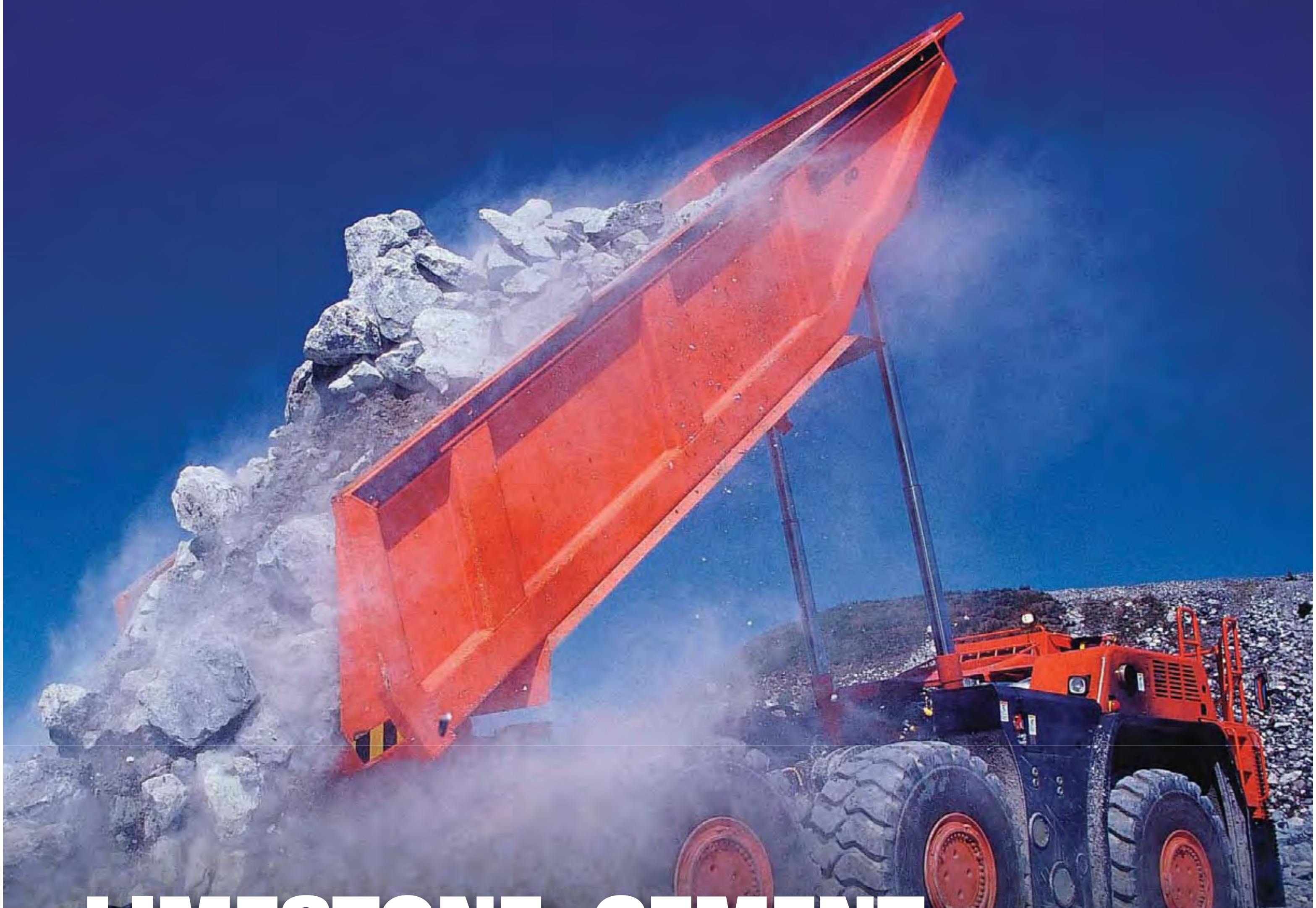

LIMESTONE, CEMENT AND CO_2 MITIGATION

IMPROVING VENTILATION IN LARGE-OPENING MINES

Special Editorial Supplement: ***2009 SME/CMA Annual Meeting Official ShowGuide***

Accelerated weathering of limestone for CO_2 mitigation: opportunities for the stone and cement industries

Large amounts of limestone fines co-produced during the processing of crushed limestone may be useful in the sequestration of carbon dioxide (CO_2). Accelerated weathering of limestone (AWL) is proposed as a low-tech method to capture and sequester CO_2 from fossil fuel-fired power plants and other point sources such as cement manufacturing. AWL reactants are readily available, inexpensive and environmentally benign. Waste CO_2 is hydrated with water to produce carbonic acid. This reacts with and is neutralized by limestone fines, thus converting CO_2 gas to dissolved calcium bicarbonate.

AWL waste products can be disposed of in the ocean.

Feasibility requires access to an inexpensive source of limestone and to seawater, thus limiting AWL facilities to within about 10 km (6 miles) of the coastline. The majority of U.S. coastal power-generating facilities are within economical transport distance of limestone resources. AWL presents opportunities for collaborative efforts among the crushed stone industry, electrical utilities, cement manufacturers and research scientists.

Fossil-fuel power plants are point source emitters of large volumes of carbon dioxide. Photo courtesy of Arnold Paul.

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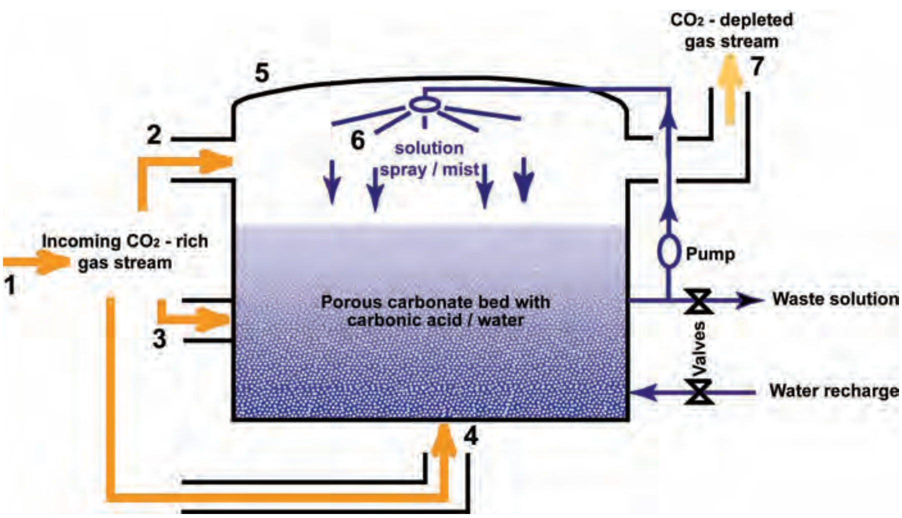
There is a concern that CO_2 generated from human activities is contributing to climatic and environmental changes. Approximately one-third of anthropogenic CO_2 emissions come from burning fossil fuels to generate electricity. Each power plant is capable of emitting several million tons of CO_2 annually. A variety of other industrial processes, such as cement manufacture, oil refining, and iron and steel production, also emit large amounts of CO_2. The level of atmospheric CO_2 can be reduced by capturing CO_2 from point-source emissions and storing or sequestering it in isolation from the atmosphere (U.S. Department of Energy, 2003). In 1999, G.H. Rau and K. Caldeira proposed a geochemistry-based method that is referred to as accelerated weathering of limestone (AWL) in a paper titled "Accelerating carbonate dissolution to sequester carbon dioxide in the ocean — geochemical implications."

Accelerated weathering of limestone

Over geologic time, the natural weathering of limestone captures and sequesters atmospheric CO_2. The AWL process speeds up the natural process by purposely bringing water in contact with limestone at a source of the CO_2 emissions to partially remove this gas from the waste gas stream. This is a low-tech strategy that does not require costly CO_2 capture, purification or pressur-

FIG. 1

An example of a possible carbonate dissolution reactor design, from Rau and Calderia (1999). A CO_2 -rich gas stream (1) enters the reactor vessel (5) by one or more entryways (e.g., 2, 3 and/or 4). The gas stream then passes over or through a wetted, porous bed of limestone particles within the reactor. This carbonate mass is sprayed (6) and wetted with, and partially submerged in, a water/carbonic acid solution that is unsaturated with respect to bicarbonate ion. This arrangement exposes the incoming gas to a large surface area of water/solution in the form of droplets and wetted carbonate particle surfaces in (5), facilitating hydration of the entering CO_2 to form a carbonic acid solution within the reactor. CO_2-depleted gas then exits the reactor (7). The carbonic acid solution formed reacts with the carbonate to form calcium and bicarbonate ions in solution, which is either recirculated or bled from the reactor and replaced with unreacted water within the reactor at a rate that maximizes benefit/cost.



ization and it is suitable for retrofitting existing power and cement plants.

During the AWL process, stack emissions with CO_2 content >5 percent by volume are passed over or through a porous bed of limestone particles wetted by a continuous spray or flow of water (Fig. 1). Carbonic acid is formed when carbon dioxide contacts the water and wetted surfaces. The acid dissolves the limestone (principally calcium carbonate), producing HCO_3- in solution.

Gaseous CO_2 is dissolved in water:

$$CO_{2(gas)} \rightarrow CO_{2(aq)} \quad (1)$$

The dissolved CO_2 is hydrated to form carbonic acid;

$$CO_{2(aq)} + H_2O \rightarrow H_2CO_{3(aq)} \quad (2)$$

Carbonic acid reacts with the solid calcium carbonate (limestone) to form Ca2+ and bicarbonate ions in solution;

$$H_2C_{O3(aq)} + CaCO_{3(solid)} \rightarrow Ca^{2+}_{(aq)} + 2HCO_{3\text{-}(aq).} \quad (3)$$

The overall reaction is, therefore:

$$CO_{2(gas)} + CaCO_{3(solid)} + H_2O \rightarrow Ca^{2+}_{(aq)} + 2HCO3_{\text{-}(aq)} \quad (4)$$

Rau and others (2007) estimate an AWL reactor volume of roughly equivalent to a 60-m (197-ft) cube could achieve a 20-percent reduction of the CO_2 emissions from a typical 500-MW coal-fired power plant. The actual required size would depend on limestone particle size and purity, water/gas/solids interaction efficiency and CO_2 concentration.

More than 9.1 kt/a (10,000 stpy) of water of CO_2 captured are required to hydrate the CO_2 and to carry and dilute the resulting bicarbonate (Rau and Caldeira, 1999). Therefore, AWL reactors will be most economical when located within 10 km (6 miles) of U.S. coastlines. About 12 percent of CO_2 emissions from U.S. electricity production occur at such power plants (Sarv and Downs, 2002). Many of those facilities are already pumping massive quantities of seawater for once-through cooling. The AWL process could conceivably make use of this “free” water prior to ocean discharge.

Proximity to potential limestone supply

Langer and others (2007) concluded that, in general, there is a sufficient supply of limestone to meet the needs of AWL and that current crushed stone technology is sufficient to produce those resources. A major variable in the final cost of AWL is the cost to transport the limestone to the point of use, which, in turn, is dependant on the distance and mode of transport. A four-step GIS exercise using three databases was conducted to determine the proximity of CO_2 point sources within the conterminous U.S. to the coast and to sources of limestone.

Digital versions of the state geologic maps (Dicken and others, 2005a, 2005b; Ludington and others, 2005; Nicholson and others, 2004, 2005, 2006; Stoeser and others, 2005) were used to locate sources of limestone. The digital geologic data include geologic formations; primary, secondary and other rock types within each formation; and lithologic descriptions of rock types. Geologic formations, as shown on geologic maps, commonly contain a variety of rock types that change across the landscape. For example, a formation at one location can contain limestone, whereas a few miles away, the same formation might not contain limestone.

The geologic information was used with CO_2 emitter and coastline data as follows:

1) The International Energy Agency Greenhouse Gas (IEA GHG) CO_2 Emissions Database (<http:// www. co2captureandstorage.info/co2emissiondatabase/ co2emissions.htm>, acquired September 2008 by written communication) was queried to select point-source emission sites within the United States, herein referred to as CO_2 point sources.

2) Proximity zones were created around the selected points and were compared with a database from the National Oceanic and Atmospheric Administration (NOAA)

(<http://shoreline. noaa. gov/data/datasheets/medres.html>, acquired October 2008) showing the U.S. coastline, to identify and select those CO_2 point sources that are within 10 km (6 miles) of the coastline. That subset of points is considered to be CO_2 point sources that could effectively use AWL.

3) The state geologic map data bases cited were searched to identify those formations that contain calcium carbonate as either the primary or secondary rock type. That subset of areas is considered to represent potential sources of carbonate rock (herein referred to as limestone) for use in AWL.

Table 1

Maximum distance from coastal point source emitter to limestone. "Other" includes manufacture of ammonia, ethylene, ethylene oxide, hydrogen, iron and steel, and oil refining.

	Distance in kilometers							
Sector	**1**	**10**	**50**	**100**	**200**	**300**	**400**	**Total**
Cement	6	2	0	0	3	0	0	11
Power	66	22	76	33	43	36	2	278
Other	16	3	19	6	43	69	2	156
Total No.	88	27	95	39	89	105	2	445
Cumulative total	88	219	379	249	338	443	445	
Cumulative total, power plants	66	165	291	197	240	276	278	

4) The distances from the CO_2 point sources to the potential sources of limestone (Table 1) were calculated by comparing the locations of the CO_2 point sources with the locations of the potential sources of limestone. The distances from power plant and cement plant CO_2 point sources to the potential sources of limestone are shown in Fig. 2.

Overall, 32 percent of the coastal power plants are within 10 km (6 miles) of potential limestone deposits; 59 percent are within 50 km (31 miles) of deposits and 71 percent are within 100 km (60 miles) of potential limestone deposits (Table 1). Because power plants constitute a large majority of CO_2 emitters and use a large amount of cooling water that may also be used in AWL, they are discussed in greater detail.

Figure 2 can be interpreted as follows: Large amounts of limestone are in the coastal areas of Florida, Georgia and the Carolinas. Many power plants in those states are within 10 km (6 miles) of potential limestone deposits and most are within 50 km (30 miles) of those deposits. Limestone resources are generally between 10 to 50 km (6 to 31 miles) of coastal power plants in New Jersey, New York and the New England states. In Virginia and Maryland, most coastal power plants are between 20 to 200 km (12 to 125 miles) from limestone deposits. In the Great Lakes, many power plants are within 10 km (6 miles) of the potential limestone deposits, except Lake Erie, where plants are generally within 200 km (125 miles) of potential deposits. Limestone resources are generally lacking near the coasts of Texas, Louisiana and Mississippi, but occur in large amounts in these states along the inland edge of the Coastal Plain, generally within 300 km (185 miles) of coastal power plants. No power plant emitters are shown within 10 km (6 miles) of the coast in Washington or Oregon. Power plants within 10 km (6 miles) of the coast in California are typically within 200 km (125 miles) of potential limestone deposits.

Limestone production and processing capabilities

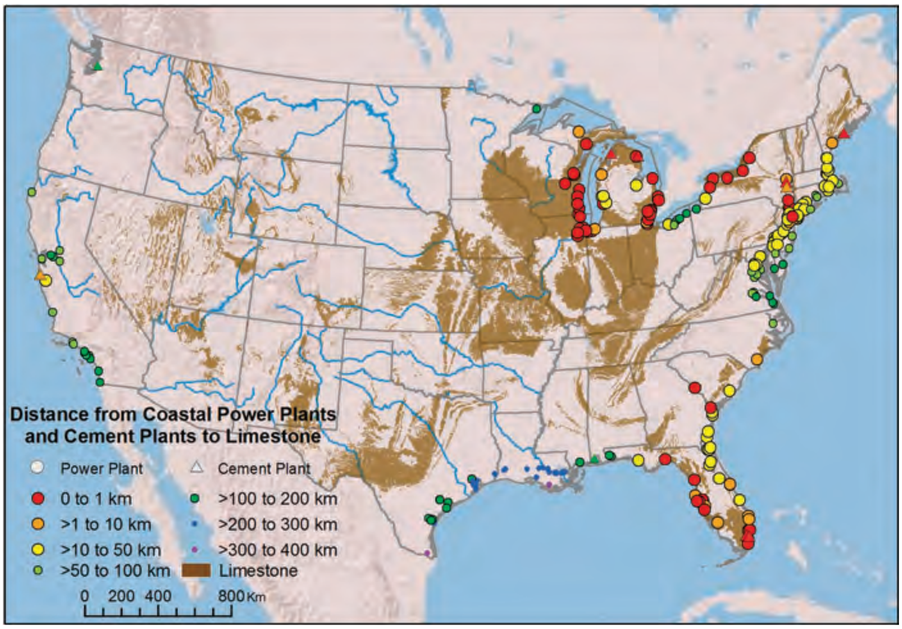
The sequestration of 1 t of CO_2 requires about 2.3 Mt of pure limestone, or 2.5 Mt of limestone with 8 percent impurities. About 2.2 Mt/a of limestone are required to sequester 20 percent of the CO_2 from a 500-MW coal-fired plant, assuming 1 t of coal produces 2.5 MW and 2.5 t of CO_2 (Rau and others, 2007).

The cheapest source of limestone would come from the waste stream of crushed limestone operations. Langer and others (2007) concluded that most, if not all, of the supply could be met from waste fines co-produced with crushed limestone aggregate. Fines are rock particles that pass through a 9.5-mm (0.4-in.) screen. Fines frequently end up as waste. The average production of fines in the limestone industry is 26 percent of annual production (Hudson and others, 1997). In some parts of Florida, only about 50 percent of the limestone delivered to the crusher may result in saleable product (McClellan and others, 2002). The remaining 50 percent is waste that could be available for AWL.

Obtaining 2.2 Mt tons of fines for AWL from the waste

FIG. 2

Distance from coastal power plants and cement plants to potential sources of limestone.



stream of crushed stone operations that produce 26 percent waste (an average plant) would require an operation that produces nearly 6.3 Mt/a of saleable limestone. Acquiring 2.2 Mt of limestone from the waste stream of crushed stone operation that produced 50 percent rock waste would require production of about 2.2 Mt/a of saleable material.

Therefore, it is feasible that AWL for a gas or coal-fired generating plant with a capacity of 500 MW could obtain the entire demand for limestone from byproduct fines and other waste limestone products from a single 5 Mt/a crushed stone operation producing 50 percent waste limestone. It would probably be necessary, however, to use byproduct fines from multiple operations, or supplement byproduct fines with a primary quarry product for operations producing 26 percent fines. Nineteen quarries in the U.S. annually produce more than 5 Mt of crushed stone and 104 quarries annually produce more than 2.5 Mt (Willett, 2007). This demonstrates that current plant capacity and technology exist to provide limestone waste for AWL at a 500-MW power plant.

Solution cavities caused by natural weathering of limestone. Photo from AGI Image Bank and Bruce Molnia, Terra Photographics.

Limestone cost

The cost of limestone varies greatly by region and use. Crusher-run (minimally processed stone used for low-specification applications) costs about $5.69 t (Willett, 2007). Cost for limestone for AWL should be significantly less if obtained as waste, or near this cost if produced specifically for AWL use.

As previously stated, most, if not all, of the supply of limestone could be met from inexpensive waste limestone fines co-produced with crushed limestone aggregate. Where the local availability of waste fines is inadequate to meet the needs for AWL, waste fines would have to be imported from other areas or limestone would have to be produced specifically for the AWL process. Limestone that is too soft, weak or impure for use as aggregate could be quarried specifically for AWL use.

Limestone transport and material handling feasibility

Langer and others (2007) concluded that the capability to transport and handle the large quantities of limestone required by AWL currently exists. They based their conclusions on the following assumptions: 1 t of coal produces 2.5 MWH; 1 t coal produces 2.5 t CO_2 ; 2.5 t 92 percent pure limestone sequesters 1 t CO_2 .

Generally, when moving small amounts of stone short distances, trucking is the preferred mode of transport. However, the volume of truck traffic for AWL would likely become problematic at the 500 MW capacity (nearly one truck every three minutes, 24 hours a day), even for a relatively short haul distance (Langer and others, 2007).

Transport of limestone by rail would be feasible for generating facilities ranging up to 1,500 MW capacity. Transportation would require more than three unit trains a day. Assuming a unit train of 110 cars with large bottom-dump hopper systems and an unloading capacity of 25 cars/hour, it would take about 4.4 hours to unload one train under ideal conditions and more than 13 hours to unload all trains. Separate rail unloading facilities could facilitate the handling of bulk material (Langer and others, 2007).

Transport of limestone by barge to a 1,500-MW capacity facility would require about 24 barges a day. The unload rate for barges ranges from 450 t to 4.5 kt/hour.

The unloading and repositioning of 24 barges a day to service a 1,500-MW capacity facility would be feasible. But, depending on the capabilities of the facility, it might be near the maximum limit (Langer and others, 2007).

Handy-size bulk freighters have a shallow draft (about 10 m or 33 ft) and a deadweight capacity of 20 to 40 kt. These freighters may be able to service some generating facilities with dockside access. They have discharge rates of about 5 kt/hour. Supplying limestone to a 1,500-MW capacity facility (with a 30-kt capacity freighter) would require slightly more than one freighter every day. Handling material for this demand is feasible (Langer and others, 2007).

Most cement operations are co-located with limestone quarries and should have the capability to handle the material required for AWL. Those cement operations that are not near limestone quarries must receive limestone as a feedstock and, therefore, are likely to have access to the necessary transportation and material handling facilities.

This type of self unloading freighter could be used to transport limestone fines from quarries with appropriate water access. Photograph courtesy AGI Image Bank and US EPA.

Environmental issues

If limestone for AWL is obtained from the waste stream of existing operations, the environmental impacts should already have been addressed by the existing operation. Using waste byproduct fines for AWL would eliminate environmental impacts resulting from opening new operations and would help alleviate a major storage problem of the crushed stone industry. Large amounts of waste stored on site at aggregate operations are unsightly and can create problems associated with dust. Removing the waste fines should improve the overall environmental status of existing crushed stone operations.

Langer and others (2007) concluded that, if limestone was quarried specifically for use in AWL, environmental impacts such as dust, noise and ground vibrations associated with mining and processing of aggregate would likely occur. Those impacts commonly would be confined to the area at or very near the quarries and could be controlled or kept within permissible limits through careful quarry planning and by employing best management practices.

Carbon footprint

For AWL to be carbon-efficient the CO_2 emitted while producing and transporting limestone to a power generating facility or cement plant that uses AWL must be less than the CO_2 sequestered by the limestone. Alcorn (2001) reports that the embodied CO_2 coefficient for crushed stone is 4.6 g/kg crushed stone. This equates to 0.01 t of CO_2 per 2.5 t of limestone production. This is the approximate amount of limestone necessary to sequester 1 t of CO_2. Furthermore, if the source of AWL limestone is from the waste stream of the crushed stone operation, the CO_2 emissions might be applied to the saleable crushed stone, resulting in zero CO_2 contribution to AWL. An alternative would be to transfer the CO_2 emissions with the fines to the AWL process, thus reducing the embodied CO_2 in the crushed stone.

The Texas Transportation Institute (2007) used the U.S. Environmental Protection Agency's MOBILE6 model (EPA, 2003) to calculate the emissions (in grams) from barge, rail and truck transport generated by moving one ton of cargo 1.6 km (1 mile). Those values, converted to grams/ton-km, are: truck – 0.0845; railroad – 0.0400; and inland waterway barge – 0.0287. The amount of CO_2 emitted to transport 2.5 t of limestone is trivial by any mode of transport. For example: transporting 2.5 t of limestone 200 km (125 miles) by truck would generate 42 grams (4.2×10^{-5} tons) of CO_2. Thus, the total CO_2 footprint to produce and transport the limestone for AWL is insignificant.

Yet another option would be to negotiate with the power plant or cement plant employing AWL for a portion of the CO_2 emissions removed by AWL. Every 2.5 t of limestone fines used to remove 1 t of CO_2 from a power plant would offset 100 t of crushed stone production. That credit could be applied to the crushed stone operation, resulting in a CO_2-neutral crushed stone operation.

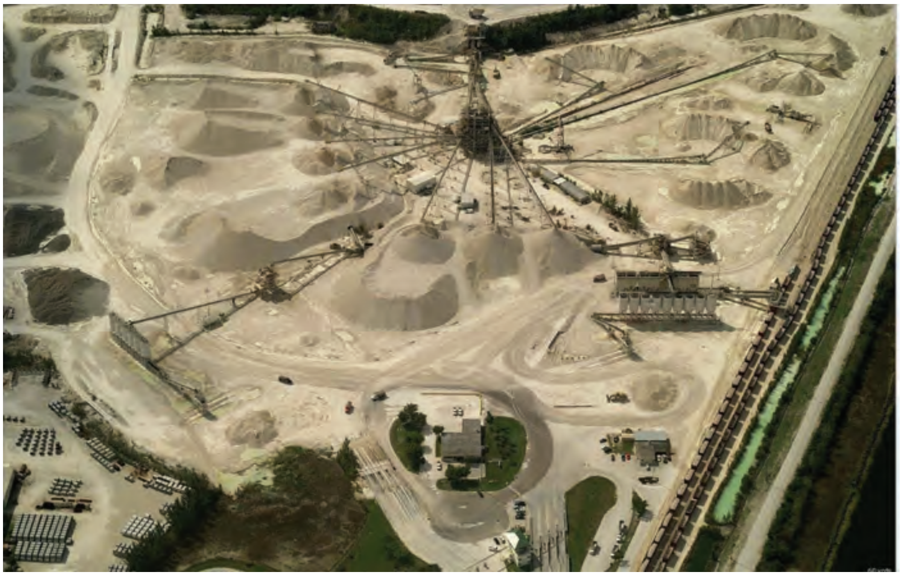
Insoluble waste

The reaction of 2.2 Mt of limestone that contains 8 percent insolubles would yield 175.2 kt of insoluble minerals. That material ultimately would be disposed of either in the ocean along with the HCO_3- solution; or back-hauled to the limestone source quarry and used as fill to recontour the mining excavations or discarded in land fills. Most of the waste is likely to be quartz, which might have industrial applications. It may also be possible to recover trace heavy minerals such as rutile and zircon (McClellan and others, 2002) from the waste.

Cost analysis

To be cost effective, AWL is limited to mitigating CO_2 point sources within about 10 km (6 miles) of the U.S. coastline. Fortuitously, 71 percent of coastal fossil fuel electric facilities are within 100 km (60 miles) of

Aggregate operations are well equipped to handle the large amounts of material required for AWL. Photo courtesy of Pictometry International Corp.



known limestone reserves, especially along the southern and eastern seaboards, which have the highest density of coastal U.S. power plants and coastal electricity-related CO_2 production. For example, Florida is mostly underlain by carbonate deposits (Scott and others, 2001) and has more than 20 GW of fossil-fueled power (about 100 Mt/d CO_2 emitted) generated by coastal power plants (Sarv and Downs, 2002). In a setting such as Florida, where limestone and transportation costs could be negligible, AWL could sequester CO_2 at a cost of about \$3 to \$4/t CO_2 (Rau and others, 2007).

The economics of AWL under three scenarios of limestone and transportation costs when using four transportation modes, is discussed below. Calculations assume 2.5 t of limestone with 8 percent impurities to mitigate 1 t of CO_2. The base capital, operating and maintenance (COM) cost is calculated where the water and limestone are obtained at no cost and is assumed to be \$4/t CO_2 mitigated (Sarv and Downs, 2002).

(1) The COM with costed limestone transport is calculated where low-grade limestone (92 percent $CaCO_3$) is supplied from quarry waste at no cost, but is transported a distance of 200 km (125 miles) using truck, unit train, barge or freighter transportation. Because 71 percent of the power plants are within a straight-line distance of 100 km (60 miles) of potential limestone, 200 km (125 miles) was chosen as a conservative shipping distance. The added cost for transport of limestone was calculated at a rate of \$0.089/t/km for truck, \$0.027/t/km for unit train, \$0.010/t/km for barge and \$0.003/t/km for freighter (Everist and Burhans, 2003). The resulting calculated costs are: truck - \$48.50; train - \$17.50; barge - \$9 and freighter - \$5.50.

(2) If limestone is purchased at a price of \$5/t (Willett, 2007). \$12.50 needs to be added to each of the preceding calculations, with the resulting mitigation costs per ton of CO_2: truck - \$61; train - \$30.00; barge - \$21.50 and freighter - \$18.

(3) Using seawater rather than recycled cooling water, and pumping it 2 vertical m (6.5 ft), adds \$4.76 to the cost (Rau and Caldeira, 1999), with the resulting mitigation costs per ton of CO_2: truck - \$65.76; train - \$34.76; barge - \$26.26 and freighter - \$22.76.

In all situations but the longest transport by truck, AWL can be cost-competitive with, or cheaper than, other forms of CO_2 capture and sequestration (Rao and Rubin, 2002; Metz and others, 2001).

Applying AWL to the cement industry

The cement manufacturing industry is a major contributor to CO_2 emissions. About 1.5 t of limestone are required to make 1 t of cement clinker. Producing 1 t of clinker results in the release of nearly 1 t of CO_2 into the atmosphere, about one-half created from calcination and one-half from burning the fossil fuels that supply the energy for calcination. Plant capacities range from less than 500 kt/a to more than 1 Mt/a (Van Oss, 2007).

Limestone is the major ingredient in cement. Consequently, clinker manufacturing plants are co-located with limestone quarries or have a system in place to economically transport limestone from the supply quarry to the plant. Reducing CO_2 emissions by 20 percent would increase limestone consumption by about 33 percent. Waste limestone of a chemical quality less than cement grade could be a ready supply for AWL, and transporting limestone for AWL should not incur significant cost.

There are 11 cement plants located in coastal areas of the U.S. (Table 1). Eight of these plants are within 10 km (6.2 miles) of limestone deposits. The other three obviously have a source of limestone within economic transport distance for cement manufacture, and may be able to use the same source and transport system for AWL.

Summary

Accelerated weathering of limestone appears to provide a low-tech, inexpensive, high-capacity, environmentally friendly CO_2 mitigation method that could be applied to about 200 fossil fuel fired power plants and about eight cement plants located in coastal areas in the conterminous U.S. This approach could also help solve the problem of disposal of limestone waste fines in the crushed stone industry. Research and implementation of this technology will require new collaborative efforts among the crushed stone and cement industries, electric utilities, and the science and engineering communities. ■

(References are available from the authors.)

Footnote

[1]Shorelines are from the National Ocean Service Navigation Charts. The shorelines are based on a vertical tidal datum, which typically is Mean Lower Low Water. Because the tidal sections of some rivers such as the Hudson River and Savannah River are classified as coastlines, some CO_2 point sources that are within 10 km (6 miles) of the coast appear to be located significantly inland from the coast.